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Master's Thesis

ENHANCED DEGRADATION OF
4-CHLOROPHENOL BY
IRON-COPPER BIMETALLIC
HOMOGENEOUS FENTON-LIKE SYSTEM

Hyungjin Jung

Department of Urban and Environmental Engineering
(Environmental Science and Engineering)

Graduate School of UNIST

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A thesis
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Hyungjin Jung

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Approved by



Advisor

Kyung Hwa Cho

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This certifies that the thesis of Hyungjin Jung is approved.

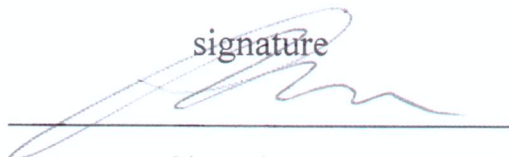
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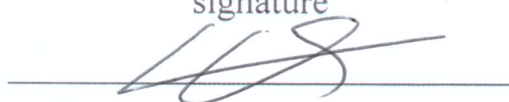
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Changha Lee

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Changsoo Lee

ABSTRACT

For decades, several recalcitrant pollutants have been continuously discharged in the aquatic systems because of the development of the industry with human activity and led to various environmental impact. Advanced oxidation processes (AOPs) have been suggested as the appropriate technology for oxidative elimination of pollutants. Fenton reaction which generates hydroxyl radical by the redox cycle of the reaction with hydrogen peroxide and ferric species has been mainly studied. However, Fenton reaction utilized at water treatment system has a limit; Fenton reaction is worked under acidic pH condition. The proper pH condition of conventional Fenton system (Fe(III)/H₂O₂ system) is near pH 3.

In order to increase the reaction pH condition, the Fe(III)/H₂O₂ and Cu(II)/H₂O₂ system were combined into the Fe(III)/Cu(II)/H₂O₂ system. In this dissertation, combined Fenton-like system (Fe(III)/Cu(II)/H₂O₂ system) was compared to conventional Fenton and Fenton-like systems (Fe(III)/H₂O₂ and Cu(II)/H₂O₂ systems) on the degradation of several recalcitrant organic compounds (benzoic acid, furfuryl alcohol, atrazine, carbamazepine, phenol, 4-chlorophenol, 3,4-dichlorophenol, 2,4,6-trichlorophenol) at pH 4 ([target compounds]₀ = 0.1 mM, [Fe(III)]₀ = [Cu(II)]₀ = 0.1 mM, [H₂O₂]₀ = 1 mM).

The rate of 4-chlorophenol degradation by the combined Fenton(-like) system was accelerated by 9-fold and 30-fold than the Fe(III)/H₂O₂ and Cu(II)/H₂O₂ systems, respectively. The Fe(III)/Cu(II)/H₂O₂ system selectively degraded phenolic compounds because the degradation products of phenolic compounds (hydroquinone and 1,2,4-benzenetriol) have substantial reducing power, which these products contribute to generating reactive oxidants by the reduction reaction of the metal ion. For identifying this mechanism, the reducing power of 4-chlorophenol degradation products was examined in the catalyst/4-chlorophenol degradation product systems, and the reduction rate of Cu(II) to Cu(I) is faster than Fe(III) to Fe(II) by each 4-chlorophenol degradation products.

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Chapter 1. Introduction

For decades, the recalcitrant pollutants like phenolic compounds and pharmaceuticals and personal care products (PPCPs) which have been emerged by the development of industry and human activity have widely affected in the aquatic systems and emerged organic contaminants which cause water pollution [1,2]. Accordingly, the water treatment methods have been also developed but the recalcitrant pollutants (phenolic compounds, and PPCPs, representatively) are difficult to be degraded by the traditional water treatment methods [3,4]. However, a few amounts of phenolic compounds and PPCPs have been continuously detected in the aquatic system [5,6]. Therefore, other water treatment methods which are more advanced than traditional technique is required.

Advanced oxidation processes (AOPs) which have been studied for the degradation of recalcitrant pollutants in aquatic systems generate powerful reactive oxygen species (ROS) such as hydroxyl radical [7] ($\cdot\text{OH}$; $E^\circ[\cdot\text{OH}/\text{H}_2\text{O}] = 2.81 \text{ V}_{\text{NHE}}$ [8]). Hydroxyl radical is generated by some processes (e.g., thermal, photochemical, electrochemical processes and direct H_2O dissociation) which have utilized various precursors and external factors [9]. However, AOPs have some limitations which are the efficiency of energy sources and operation cost, compared with other treatment processes [10-12].

Among them, this study focuses on the Fenton system in thermal processes. In the Fenton system, hydroxyl radical is generated by the redox cycle of the reaction of H_2O_2 with Fe(III)/Fe(II) , which is called the Haber-Weiss mechanism (Figure 1.1) [13]. In this mechanism, Fenton reaction which is known as generating hydroxyl radical is worked under acidic condition via the one-electron transfer reaction [14,15]. The rate of the reaction which Fe(III) is reduced to Fe(II) by the reaction with H_2O_2 is much slower than Fe(II) is oxidized to Fe(III) , generating hydroxyl radical [16]. First step reaction is the rate-determining step (RDS) and cause of Fe(III) accumulation [17]. In neutral pH, the efficiency of Fenton system is substantially decreased because Fe(III) and Fe(II) are precipitated in the aquatic systems and ferryl ion [18,19] (Fe(IV) ; generated by the reaction with H_2O_2 and iron species via two-electron transfer reaction) is generated to be difficult to degrading organic pollutants (Figure 1.2).

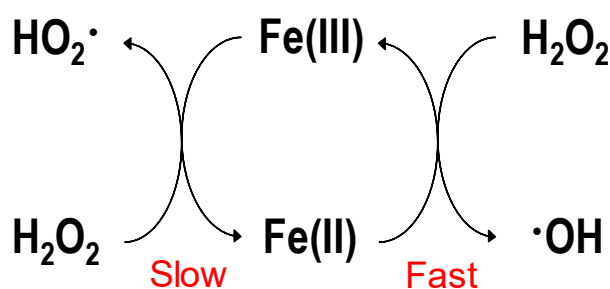


Figure 1.1. Scheme of Haber-Weiss mechanism

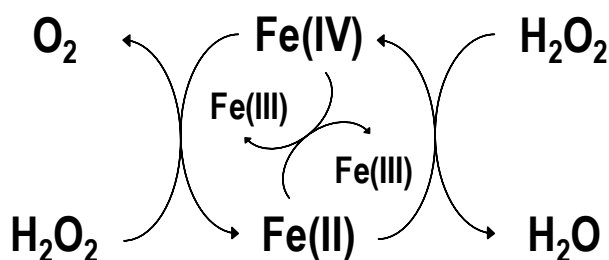


Figure 1.2. Scheme of non-radical mechanism

Recently, copper species show that copper-Fenton reaction can also generate reactive oxidant by the redox cycle of the reaction of H_2O_2 with Cu(II)/Cu(I) and this Fenton-like reaction is influenced by pH condition (under neutral and alkaline pH) [14,15,20]. Also, this Fenton-like system have been studied for inactivating microorganisms and controlling biofouling of membrane [21-23]. In the copper-catalyzed Fenton-like system, the cupryl ion (Cu(III)) is a dominant reactive oxidant for degrading organic compounds (Figure 1.3) [15,24].

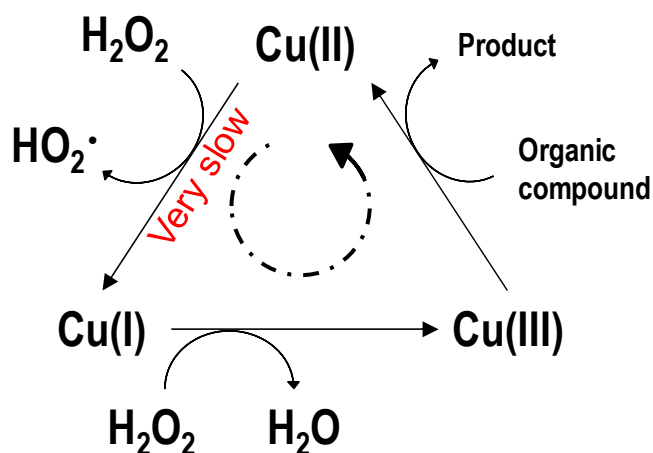


Figure 1.3. Scheme of copper-catalyzed Fenton-like mechanism

In the single metal ion catalyst/ H_2O_2 systems, the reaction which Fe(III) and Cu(II) are reduced to Fe(II) and Cu(I) by H_2O_2 is the rate-determining step for the generation of reactive oxidants [15,16,24]. Because the rate of these steps is so slow, the $\text{Fe(III)/H}_2\text{O}_2$ and $\text{Cu(II)/H}_2\text{O}_2$ systems are difficult to degrade several recalcitrant pollutants. In order to improve the rate of pollutants degradation, both systems are combined into the $\text{Fe(III)/Cu(II)/H}_2\text{O}_2$ system. The $\text{Fe(III)/Cu(II)/H}_2\text{O}_2$ system shows the enhancement of phenolic compounds degradation compared with the $\text{Fe(III)/H}_2\text{O}_2$ and $\text{Cu(II)/H}_2\text{O}_2$ systems at pH 4. From the previous studies, there are no coupling reactions between Fe(III) and Cu(II) in the combined Fenton-like system. Therefore, the enhancement at this system is believed to the result

of each role of Fe(III) and Cu(II), which is related to the phenolic compounds. However, the information about the relation between Fe(III) and Cu(II), the concentration of reagents, and the detailed mechanism has not been reported on the degradation of phenolic compounds by the Fe(III)/Cu(II)/H₂O₂ system.

The objectives of this study are to assess the potential of the Fe(III)/Cu(II)/H₂O₂ system for oxidation of organic compounds and to discuss the role of Fe(III) and Cu(II) for producing reactive oxidants. The Fe(III)/Cu(II)/H₂O₂ system is compared to the Fe(III)/H₂O₂ and Cu(II)/H₂O₂ systems (conventional Fenton(-like) system) under different pH condition and the dose of reagents. The main target compound is 4-chlorophenol, but also the degradation of other organic compounds was examined, such as benzoic acid, furfuryl alcohol, atrazine, carbamazepine, phenol, 3,4-dichlorophenol, 2,4,6-trichlorophenol. In addition, the reducing power of the 4-chlorophenol degradation products was also examined, which would provide insight into investigating the mechanism for producing reactive oxidants (hydroxyl radical and cupryl ion).

Chapter 2. Materials and Methods

2.1. Reagents

All chemicals were of reagent grade and used without further purification. Chemicals used in this work include iron(III) perchlorate hydrate, copper(II) sulfate, H_2O_2 (30 wt. % in H_2O), perchloric acid (HClO_4), sodium hydroxide (NaOH), 4-chlorophenol (4-CP), benzoic acid (BA), furfuryl alcohol (FFA), carbamazepine (CBZ), phenol, 3,4-dichlorophenol (3,4-DCP), 2,4,6-trichlorophenol (2,4,6-TCP), hydroquinone (HQ), 1,2,4-benzenetriol (BT) (all from Sigma-Aldrich Co.) and atrazine (AT) (Fluka co.). All stock solutions were prepared using deionized water (18 $\text{M}\Omega\cdot\text{cm}$ Milli-Q water from a Millipore system). A Fe(III) stock solution (10 mM) was prepared by dissolving iron(III) perchlorate hydrate in a 0.1 M HClO_4 solution. Stock solutions of Cu(II) (10 mM), H_2O_2 (1 M), 4-chlorophenol (4-CP, 10 mM), benzoic acid (BA, 10 mM), furfuryl alcohol (FFA, 10 mM), atrazine (AT, 0.125 mM), carbamazepine (CBZ, 0.125 mM), phenol (10 mM), 3,4-dichlorophenol (3,4-DCP, 1 mM), 2,4,6-dichlorophenol (2,4,6-TCP, 1 mM) were prepared and stored at 4 °C until use. Also, follow stock solutions was prepared with pure N_2 sparged DI water: hydroquinone (HQ, 10 mM), 1,2,4-benzenetriol (BT, 10 mM).

2.2. Experimental setup and procedure

All experiments were performed in a 125 mL Erlenmeyer flask (50 mL of reaction solution) open to the atmosphere at room temperature (22 ± 2 °C). The solution pH was adjusted using 1 N HClO_4 and 1 N NaOH and the variation of solution pH was less than 0.1 units during the reaction. In these experiments, each system was initiated by adding an aliquot of the metal ion catalyst (Fe(III) or Cu(II)) stock solution to a pH-adjusted solution containing target organic compounds (4-CP, BA, FFA, AT, CBZ, phenol, 3,4-DCP, 2,4,6-TCP, respectively) and H_2O_2 . Reaction samples (1 mL) were withdrawn at predetermined time intervals and were immediately quenched by adding 20 μL methanol. All experiments were performed at least in duplicate, and the average values with standard deviations were presented. Basic condition of these experiments is as in the following: $[\text{Target organic compounds}]_0 = 0.1$ mM, $[\text{Fe(III)}]_0 = [\text{Cu(II)}]_0 = 0.1$ mM, $[\text{H}_2\text{O}_2]_0 = 10$ mM, and $\text{pH} = 4.0$. For several experiments, the concentration of target organic compound (mainly 4-CP), metal ion catalyst, and pH were changed in the ranges of 0.01 – 0.1 mM, 0.01 – 0.1 mM, and 3.0-5.5, respectively. For investigating reducing power of 4-CP degradation products (HQ, BT), these products were injected into metal ion catalyst solution ($[\text{HQ}]_0 = [\text{BT}]_0 = 0.1$ mM, $[\text{Fe(III)}]_0 = [\text{Cu(II)}]_0 = 0.1$ mM) and samples (1 mL) were withdrawn at predetermined time intervals and immediately reacted with colorimetric determination reagents to figure out metal ions reduced by 4-CP degradation products.

2.3. Analytical methods

The concentrations of the target organic compounds were measured by rapid separation liquid chromatography (RSLC, UltiMate 3000, Dionex Co., U.S.A.) with UV absorbance detection (at 230, 227, 220, 220, 285, 277, 230 and 230 nm for 4-CP, BA, FFA, AT, CBZ, phenol, 3,4-DCP, 2,4,6-TCP, respectively). The chromatographic separation was performed on a 2.1 mm \times 150 mm, 5 μ m 120Å C18 column (Acclaim™ 120 C18 column, ThermoFisher Scientific Inc., U.S.A.) using a 0.1 % aqueous solution of phosphoric acid and neat acetonitrile as the eluent at a flow rate of 0.8 mL/min except CBZ analysis (with phosphoric acid solution, methanol, and acetonitrile). The concentrations of H₂O₂, Fe(II) and Cu(I) were measured by a spectrophotometer (Lambda 465, Perkin-Elmer Inc., U.S.A.) using titanium sulfate method ($\epsilon_{405} = 730 \text{ M}^{-1}\text{s}^{-1}$;[25]), 1,10-phenanthroline method ($\epsilon_{510} = 11050 \text{ M}^{-1}\text{s}^{-1}$;[26]) and DMP method ($\epsilon_{454} = 7650 \text{ M}^{-1}\text{s}^{-1}$;[27]), respectively.

Chapter 3. Results and Discussion

3.1. Results

3.1.1. Degradation of 4-CP by the catalyst/H₂O₂ systems in various pH condition

The degradation of 4-CP by Fenton(-like) system was significantly affected by the solution pH because the hydroxyl radical generation mechanism depends on pH condition [14]. The Fe(III)/H₂O₂ system did perfectly degrade all 4-CP at pH 3.0 and 3.5 in 30 minutes (Figure 3.1a). Whereas, the Fe(III)/H₂O₂ system at pH 4.0 to 5.5 and the Cu(II)/H₂O₂ system at pH 3.0 to 5.5 hardly degraded 4-CP (Figure 3.1a and 3.1b). In the case of the Fe(III)/Cu(II)/H₂O₂ system, at pH 4.5 to 5.5 range, the 4-CP was not degraded like other systems. At pH 4, the degradation of 4-CP by the Fe(III)/Cu(II)/H₂O₂ system (90% degradation in 2 h) was much higher than the sum of the 4-CP degradation by the Fe(III)/H₂O₂ and Cu(II)/H₂O₂ systems (approximately 13% degradation: 10% degradation by the Fe(III)/H₂O₂ system and 3% degradation by the Cu(II)/H₂O₂ system in 2 h) (Figure 3.1c). Comparing the Fe(III)/Cu(II)/H₂O₂ system and the sum of the Fe(III)/H₂O₂ and Cu(II)/H₂O₂ systems at pH 3.0 and 3.5 (Figure 3.1a and 3.1b versus Figure 3.1c), the 4-CP degradation rate was higher in the Fe(III)/Cu(II)/H₂O₂ system than the sum of the Fe(III)/H₂O₂ and Cu(II)/H₂O₂ systems (approximately 40% degradation versus 13%, 2% degradation, respectively in 10 min).

To figure out the enhancement degree of two metal ion catalysts (Fe(III) and Cu(II)), the enhancement rate (i.e., $\Delta[4\text{-CP}]_{\text{Fe(III)/Cu(II)}} / (\Delta[4\text{-CP}]_{\text{Fe(III)}} + \Delta[4\text{-CP}]_{\text{Cu(II)}})$) was calculated from the results of Figure 3.1 (Figure 3.2). This rate was calculated using the data points of 10 min 4-CP concentration at pH 3.0 and 3.5, and 120 min 4-CP concentration over pH 4.0. The enhancement rate of 4-CP degradation was the highest at pH 4, which increased as pH increased at pH 3.0 to 4.0 range and dramatically decreased as pH increased at over pH 4.0.

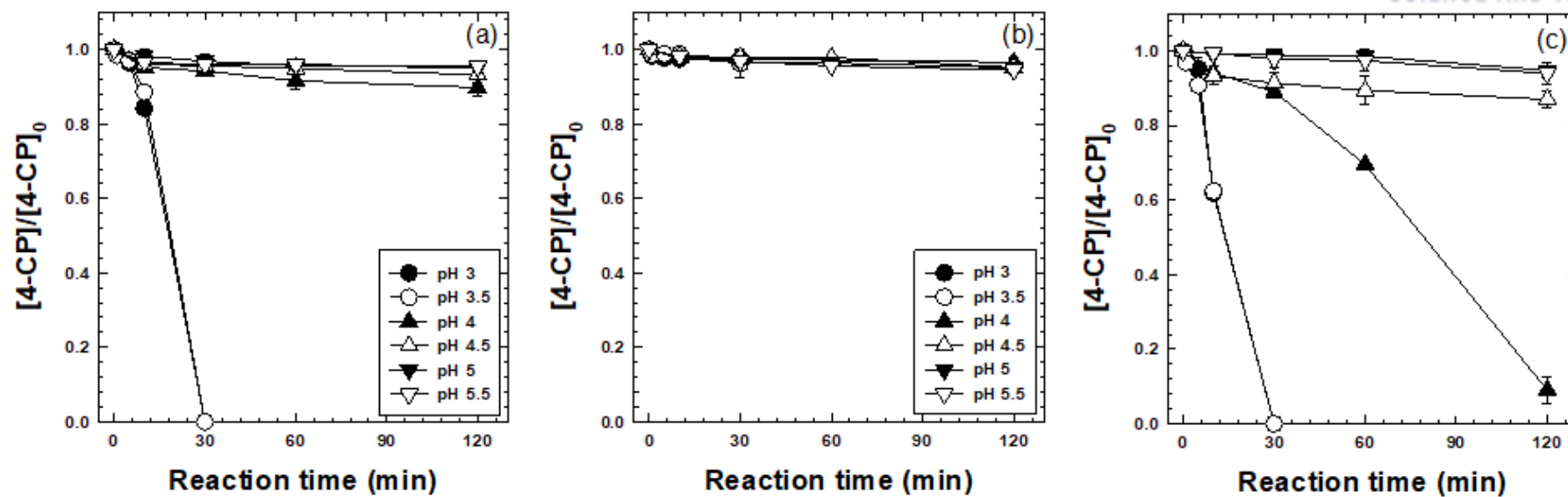


Figure 3.1. Degradation of 4-chlorophenol by the Fe(III)/H₂O₂ (a), Cu(II)/H₂O₂ (b) and Fe(III)/Cu(II)/H₂O₂ (c) systems at various pH conditions ($[4-CP]_0 = 0.1$ mM; $[Fe(III)]_0 = [Cu(II)]_0 = 0.1$ mM; $[H_2O_2]_0 = 1$ mM)

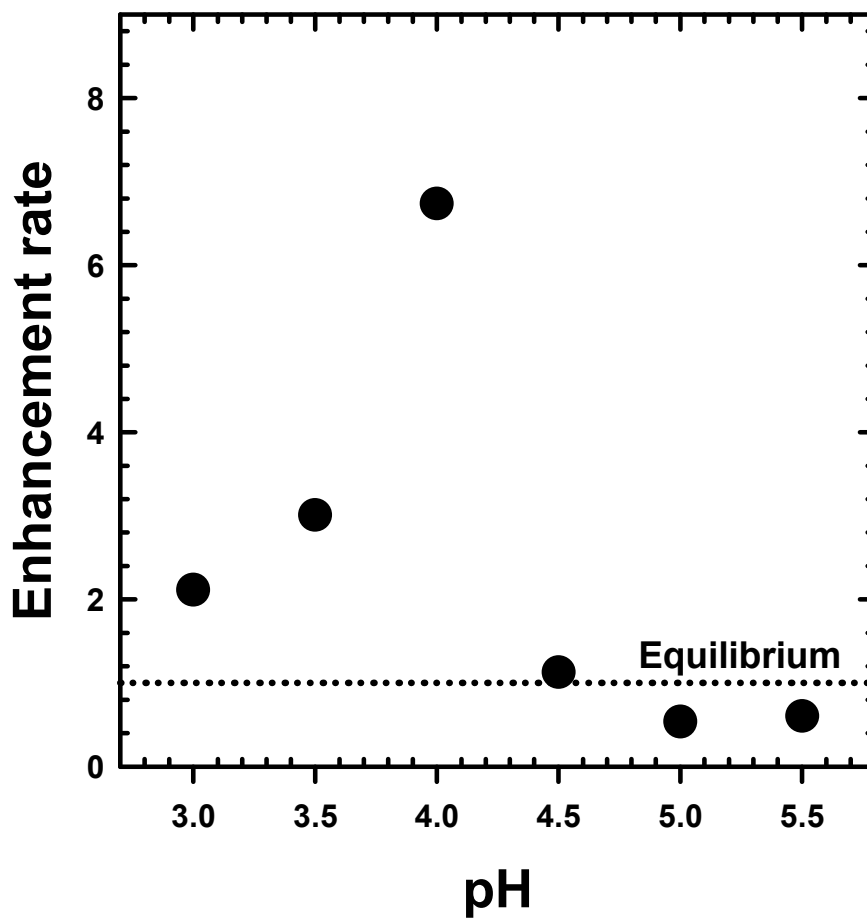


Figure 3.2. Calculated enhancement rate of 4-chlorophenol degradation by the metal ion catalyst/H₂O₂ systems at various pH conditions ([4-CP]₀ = 0.1 mM; [Fe(III)]₀ = [Cu(II)]₀ = 0.1 mM; [H₂O₂]₀ = 1 mM)

3.1.2. Effects of 4-CP and catalysts concentration

The effect of 4-CP concentration on the degradation of 4-CP was examined in the Fe(III)/H₂O₂, Cu(II)/H₂O₂ and Fe(III)/Cu(II)/H₂O₂ systems at pH 4 (Figure 3.3). The Fe(III)/H₂O₂ system under 10 μ M and 25 μ M 4-CP concentration degraded approximately 30 % and 20 % 4-CP in 2 h, respectively. In the other 4-CP concentration conditions, this system degraded 10 % 4-CP in 2 h (Figure 3.3a). The Cu(II)/H₂O₂ system did not degrade 4-CP (Figure 3.3b). In the Fe(III)/Cu(II)/H₂O₂ system, the degradation of 4-CP under 10 μ M concentration shows the similar degradation amount with the Fe(III)/H₂O₂ system. Whereas, in other condition, the amount of 4-CP degradation was gradually increased depending on the increase initial concentration of 4-CP. The enhancement rate of 4-CP degradation under 4-CP concentration was calculated from the results of Figure 3.3 (Figure 3.4). The enhancement rate increased as the concentration of 4-CP increased.

The concentration of metal ion catalysts influenced the 4-CP degradation by the Fe(III)/Cu(II)/H₂O₂ system (Figure 3.5). For comparing the effect of each metal ion concentration, the concentration of Fe(III) or Cu(II) was fixed on 0.1 mM at each experiment. When the concentration of Cu(II) was 10 μ M, the degradation of 4-CP was negligible. However, when the concentration of Cu(II) was 50 and 100 μ M, all 4-CP was degraded by the Fe(III)/Cu(II)/H₂O₂ system (Figure 3.5a). In the case of adjusting Fe(III) concentration, the degradation of 4-CP was increased as the increase of initial Fe(III) concentration (Figure 3.5b). The enhancement rate of 4-CP degradation in which Cu(II) concentration was 0.1 mM (adjusting Fe(III) concentration) tended to increase according to increase the initial concentration of Fe(III) (Figure 3.6).

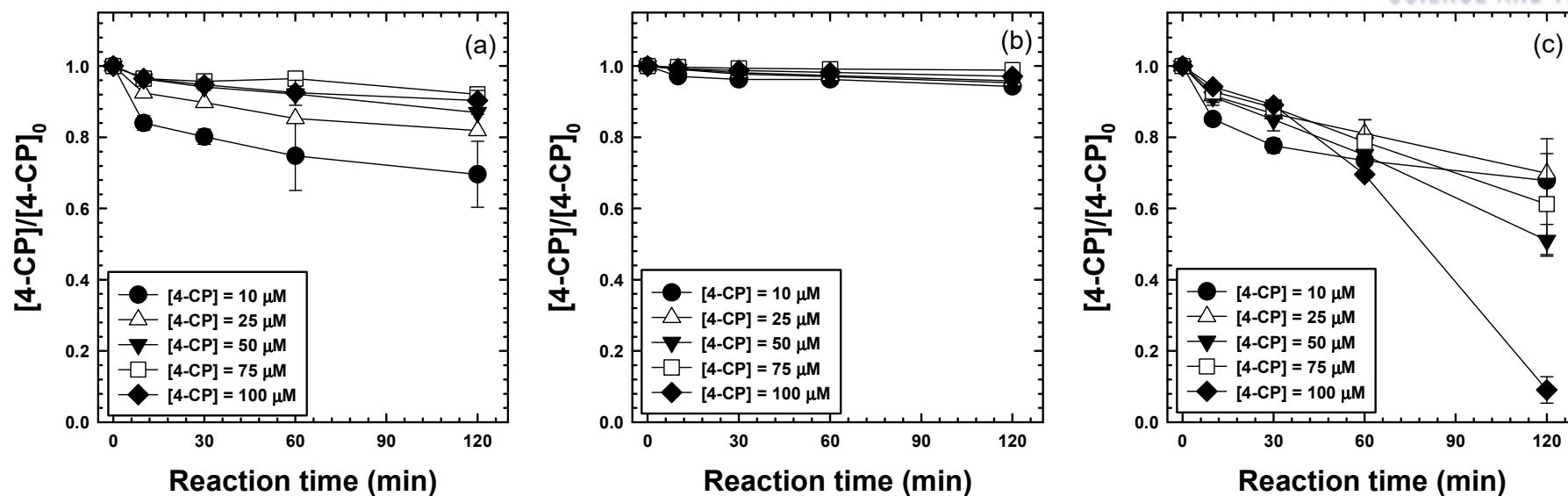


Figure 3.3. Degradation of 4-chlorophenol under target concentration change by the Fe(III)/H₂O₂ (a), Cu(II)/H₂O₂ (b) and Fe(III)/Cu(II) /H₂O₂ (c) systems at pH 4 ([Fe(III)]₀ = [Cu(II)]₀ = 0.1 mM; [H₂O₂]₀ = 1 mM)

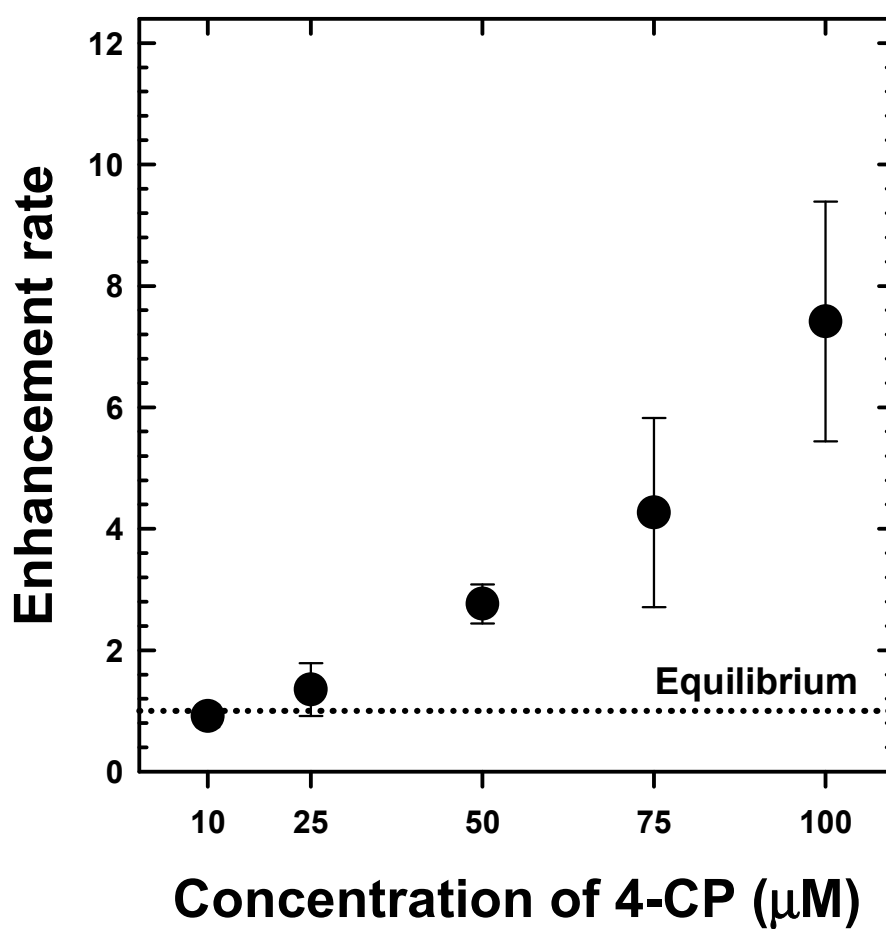


Figure 3.4. Calculated enhancement rate of 4-chlorophenol degradation under target concentration change by the metal ion catalyst/H₂O₂ systems at pH 4 ([Fe(III)]₀ = [Cu(II)]₀ = 0.1 mM; [H₂O₂]₀ = 1 mM)

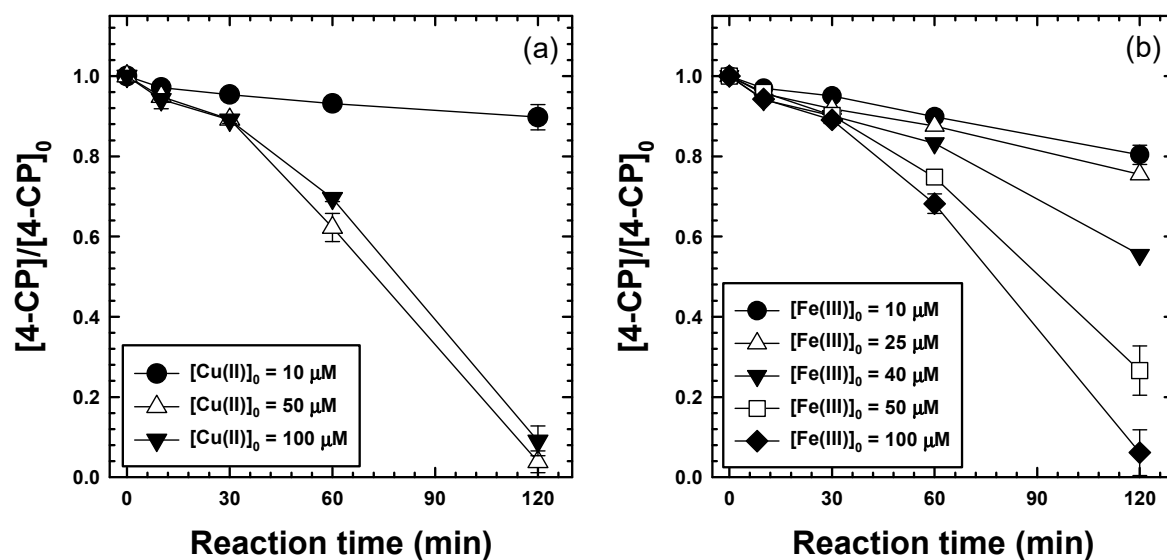


Figure 3.5. Effect of initial concentration of Cu(II) (a) and Fe(III) (b) on the 4-chlorophenol degradation by the Fe(III)/Cu(II)/H₂O₂ systems at pH 4 ($[4-CP]_0 = 0.1$ mM; $[Fe(III)]_0 = 0.1$ mM (a); $[Cu(II)]_0 = 0.1$ mM (b); $[H_2O_2]_0 = 1$ mM)

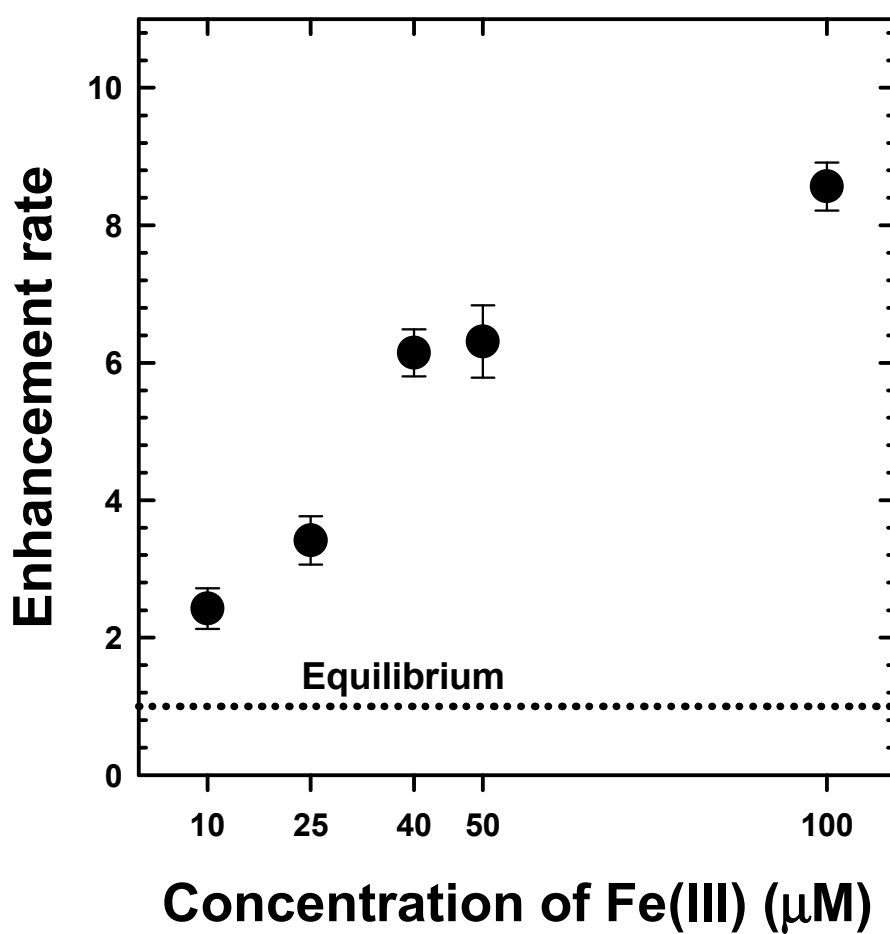


Figure 3.6. Calculated enhancement rate of 4-chlorophenol degradation by the Fe(III)/Cu(II)/H₂O₂ systems under Fe(III) concentration change at pH 4 ([4-CP]₀ = 0.1 mM; [Cu(II)]₀ = 0.1 mM; [H₂O₂]₀ = 1 mM)

3.1.3. Degradation of various organic compounds

Degradation of various organic compounds (4-CP, BA, FFA, AT, and CBZ) was tested in the metal ion catalyst/H₂O₂ systems at pH 4 (Figure 3.7). Except for 4-CP, all organic compounds were not degraded by the Fe(III)/H₂O₂, Cu(II)/H₂O₂, and Fe(III)/Cu(II)/H₂O₂ systems. In addition, H₂O₂ decomposition showed a similar trend with organic compounds degradation (Figure 3.8). The degradation of 4-CP by the metal ion catalyst/H₂O₂ system had the highest enhancement rate value, and the value of the other enhancement rate was near or less than 1 (Figure 3.9).

The degradation of several phenolic compounds (phenol, 4-CP, 3,4-DCP, 2,4,6-TCP) was also examined by the metal ion catalyst/H₂O₂ systems (Figure 3.10). The Fe(III)/H₂O₂ system could degrade approximately 10 % of all phenolic compounds respectively (Figure 3.10a), and the Cu(II)/H₂O₂ system hardly degraded each phenolic compound (Figure 3.10b). Comparing the degradation of phenolic compounds by the Fe(III)/Cu(II)/H₂O₂ system (Figure 3.10c), the 4-CP degradation was the highest, followed by 3,4-DCP, phenol, and 2,4,6-TCP, respectively. The decomposition of H₂O₂ on phenolic compounds degradation by the metal ion catalyst/H₂O₂ systems showed a similar trend with phenolic compounds degradation by all systems (Figure 3.11). The enhancement rate of several phenolic compounds degradation was presented in the same order in which the phenolic compounds were degraded by the Fe(III)/Cu(II)/H₂O₂ system (Figure 3.12).

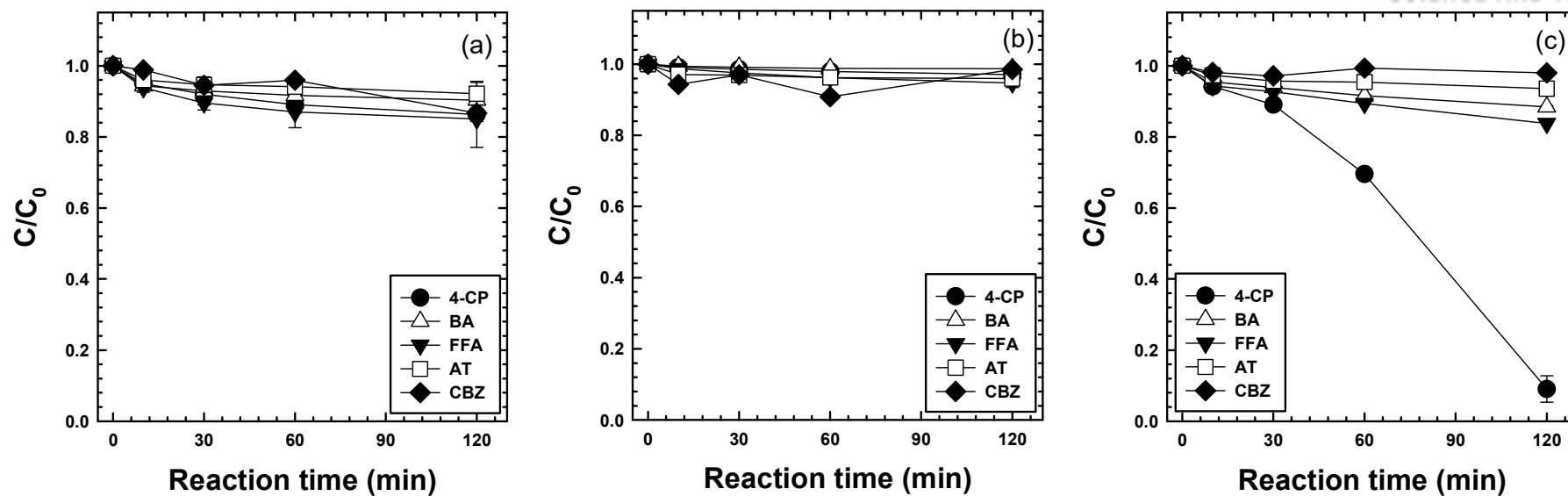


Figure 3.7. Degradation of various organic compounds by the Fe(III)/H₂O₂ (a), Cu(II)/H₂O₂ (b) and Fe(III)/Cu(II)/H₂O₂ (c) systems at pH 4 ([4-CP]₀ = [BA]₀ = [FFA]₀ = [AT]₀ = [CBZ]₀ = 0.1 mM; [Fe(III)]₀ = [Cu(II)]₀ = 0.1 mM; [H₂O₂]₀ = 1 mM)

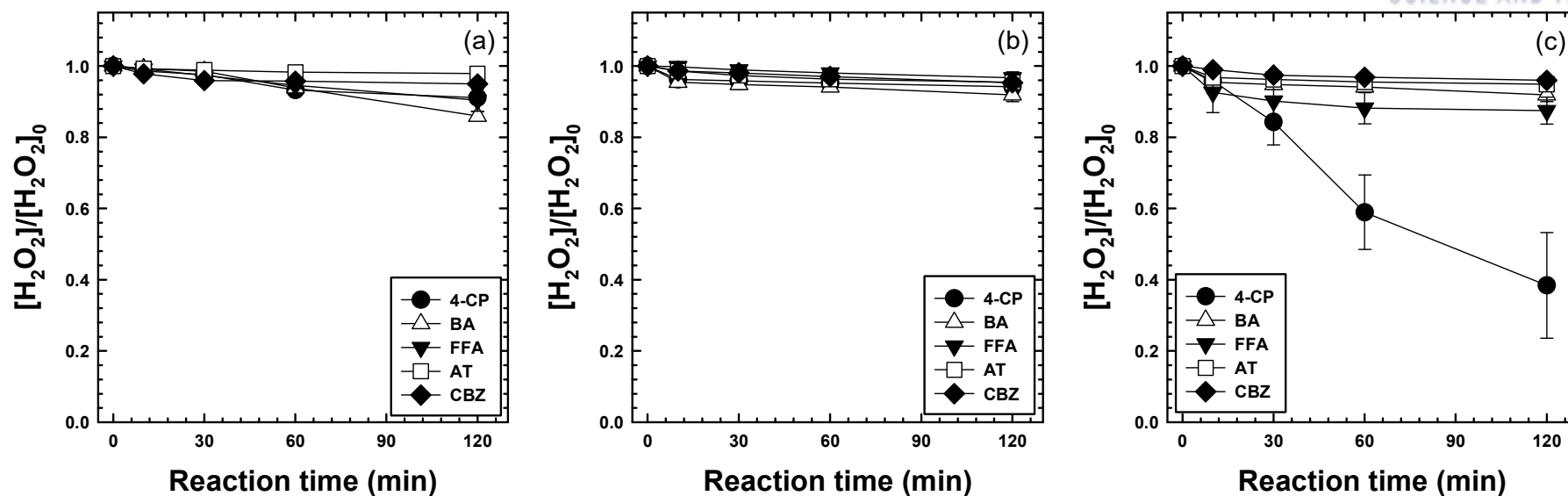


Figure 3.8. Decomposition of H_2O_2 in the $\text{Fe(III)/H}_2\text{O}_2$ (a), $\text{Cu(II)/H}_2\text{O}_2$ (b) and $\text{Fe(III)/Cu(II)/H}_2\text{O}_2$ (c) systems at pH 4 ($[\text{4-CP}]_0 = [\text{BA}]_0 = [\text{FFA}]_0 = [\text{AT}]_0 = [\text{CBZ}]_0 = 0.1 \text{ mM}$; $[\text{Fe(III)}]_0 = [\text{Cu(II)}]_0 = 0.1 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$)

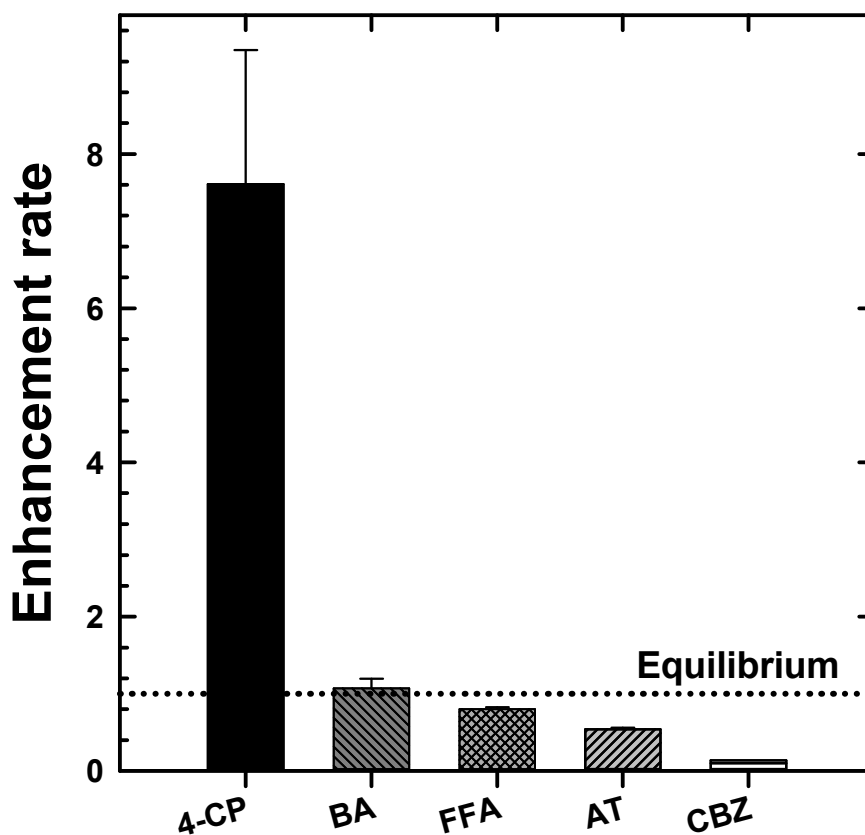


Figure 3.9. Calculated enhancement rate of various organic compounds degradation by the metal ion catalyst/H₂O₂ systems at pH 4 ([4-CP]₀ = [BA]₀ = [FFA]₀ = [AT]₀ = [CBZ]₀ = 0.1 mM; [Fe(III)]₀ = [Cu(II)]₀ = 0.1 mM; [H₂O₂]₀ = 1 mM)

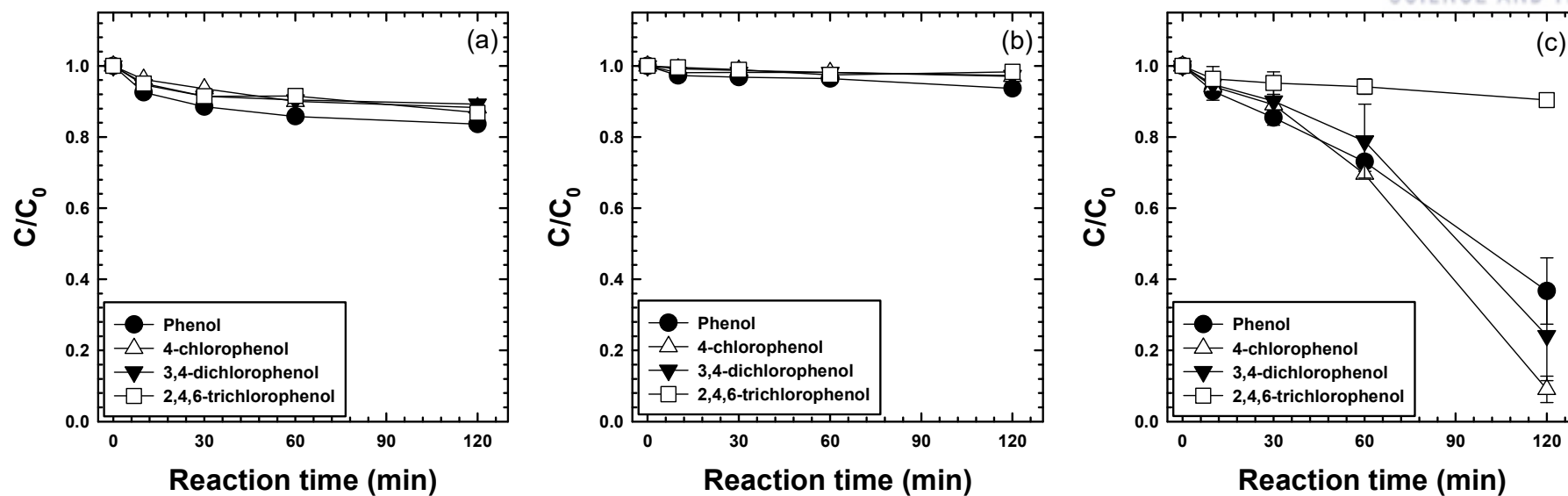


Figure 3.10. Degradation of phenolic compounds by the Fe(III)/H₂O₂ (a), Cu(II)/H₂O₂ (b) and Fe(III)/Cu(II)/H₂O₂ (c) systems at pH 4 ([Phenol]₀ = [4-CP]₀ = [3,4-DCP]₀ = [2,4,6-TCP]₀ = 0.1 mM; [Fe(III)]₀ = [Cu(II)]₀ = 0.1 mM; [H₂O₂]₀ = 1 mM)

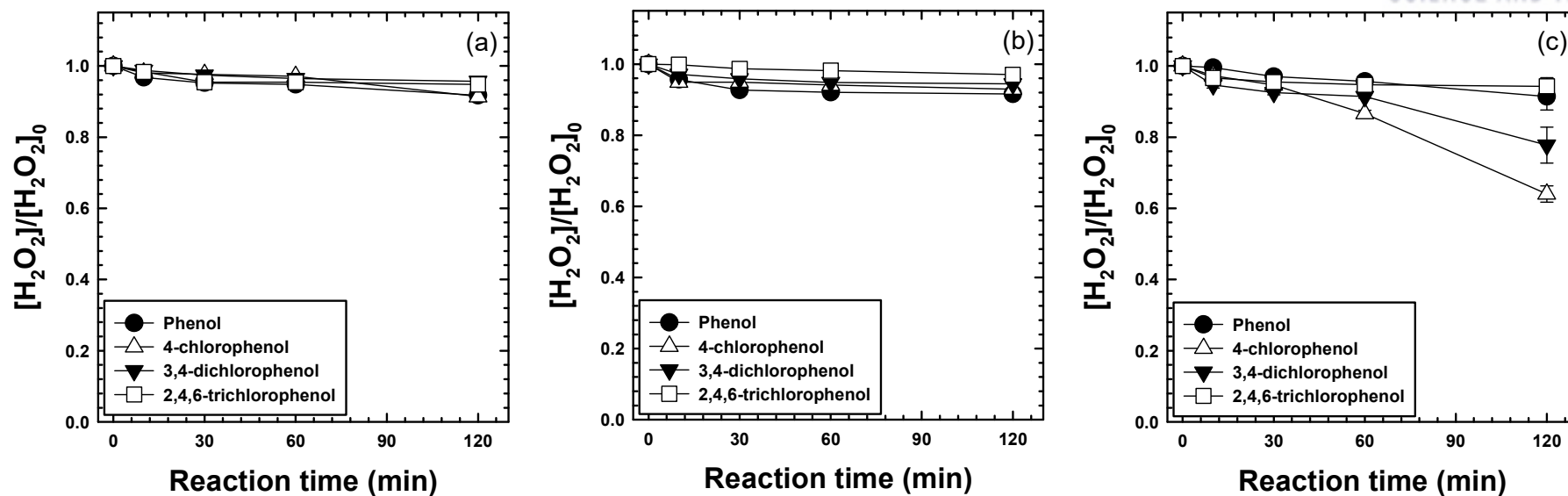


Figure 3.11. Decomposition of H_2O_2 in the Fe(III)/ H_2O_2 (a), Cu(II)/ H_2O_2 (b) and Fe(III)/Cu(II)/ H_2O_2 (c) systems at pH 4 ($[\text{Phenol}]_0 = [\text{4-CP}]_0 = [\text{3,4-DCP}]_0 = [\text{2,4,6-TCP}]_0 = 0.1 \text{ mM}$; $[\text{Fe(III)}]_0 = [\text{Cu(II)}]_0 = 0.1 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$)

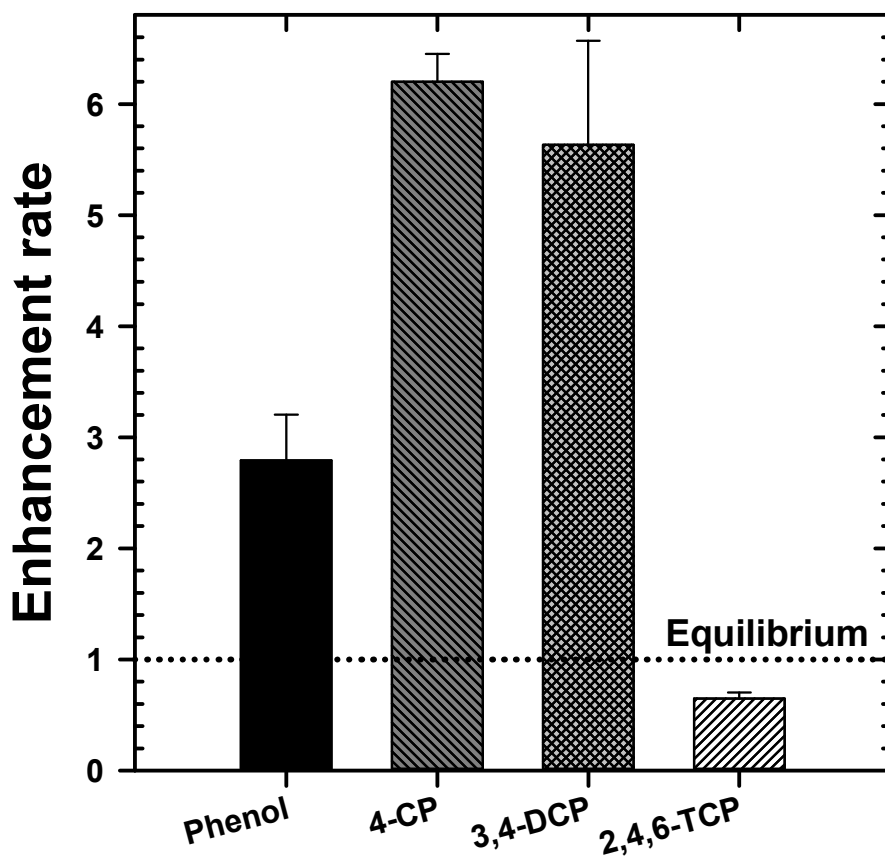


Figure 3.12. Calculated enhancement rate of phenolic compounds degradation by the metal ion catalyst/ H_2O_2 systems at pH 4 ($[\text{Phenol}]_0 = [\text{4-CP}]_0 = [\text{3,4-DCP}]_0 = [\text{2,4,6-TCP}]_0 = 0.1 \text{ mM}$; $[\text{Fe(III)}]_0 = [\text{Cu(II)}]_0 = 0.1 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$)

3.1.4. Degradation products of phenolic compounds and the effect of these

Hydroquinone (HQ) and benzoquinone (BQ) are fundamental degradation products of phenol and 4-CP [28]. The production of BQ was examined in the metal ion catalyst/H₂O₂ systems at pH 4 (Figure 3.13). The Fe(III)/H₂O₂ and Cu(II)/H₂O₂ systems hardly produced BQ (0.7 ~ 1.5 μM on the degradation of phenol and 4-CP in 2 h) (Figure 3.13a and 3.13b). The degradation of phenol and 4-CP by the Fe(III)/Cu(II)/H₂O₂ system produced 20 μM and 5 μM of BQ in 2 h (Figure 3.13c). If two metal ion catalysts coexisted together in the metal ion catalyst/H₂O₂ system, the production of BQ was dramatically enhanced. In addition, the HQ was also examined but was not measured in the metal ion catalyst/H₂O₂ systems.

To investigating the effects of several phenolic compounds degradation products, the reducing power of the products was examined (Figure 3.14); Fe(III) or Cu(II) was reacted with hydroquinone (HQ) and 1,2,4-benzenetriol (BT). Most of Fe(III) was reduced to Fe(II) in 60 sec by HQ and in 10 sec by BT (Figure 3.14a), also Cu(II) was reduced to Cu(I) in 10 sec by HQ and was immediately reduced to Cu(I) by BT. Besides, the rate of the reducing Cu(II) to Cu(I) by two degradation products was much faster than the reducing Fe(III) to Fe(II).

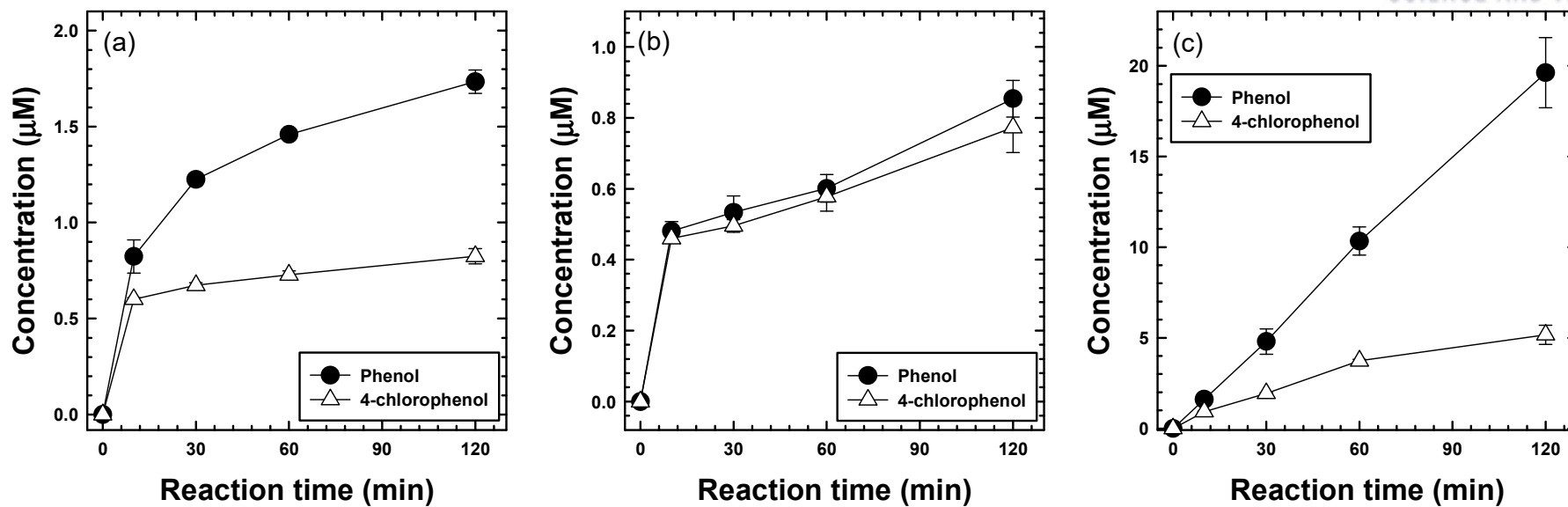


Figure 3.13. Production of benzoquinone on phenolic compounds degradation by the $\text{Fe(III)}/\text{H}_2\text{O}_2$ (a), $\text{Cu(II)}/\text{H}_2\text{O}_2$ (b) and $\text{Fe(III)}/\text{Cu(II)}/\text{H}_2\text{O}_2$ (c) systems at pH 4 ($[\text{Phenol}]_0 = [\text{4-CP}]_0 = 0.1 \text{ mM}$; $[\text{Fe(III)}]_0 = [\text{Cu(II)}]_0 = 0.1 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 1 \text{ mM}$)

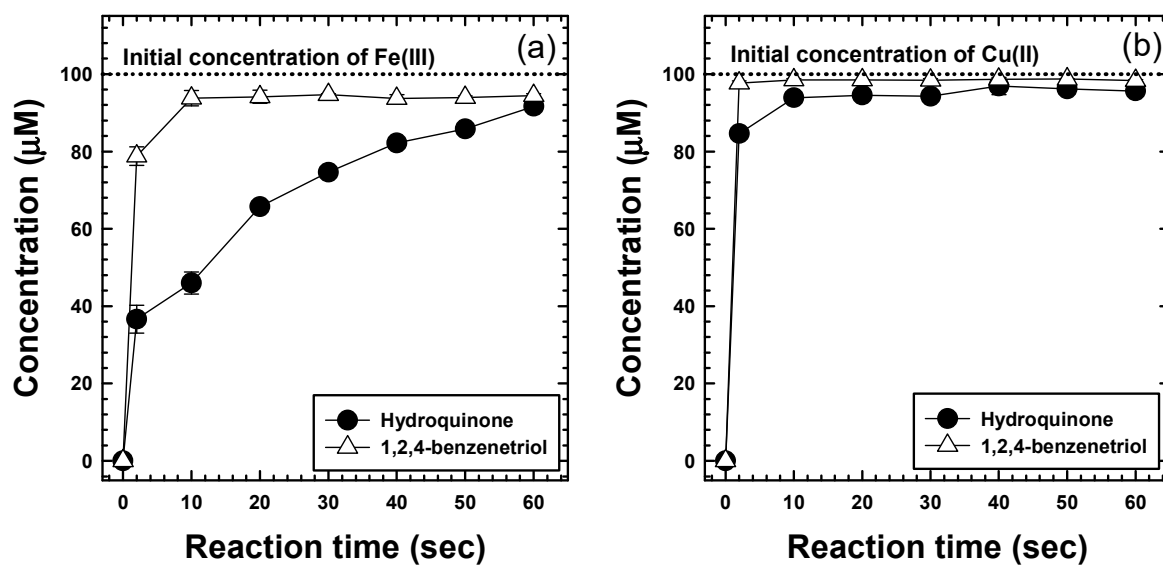
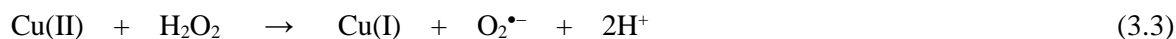
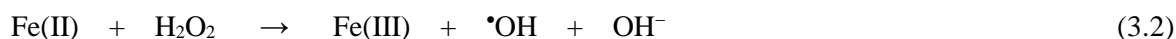
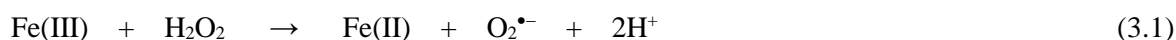


Figure 3.14. Concentration of Fe(II) (a) and Cu(I) (b) produced by catalyst/4-chlorophenol degradation product systems ($[\text{Hydroquinone}]_0 = [\text{1,2,4-benzenetriol}]_0 = 0.1 \text{ mM}$; $[\text{Fe(III)}]_0 = [\text{Cu(II)}]_0 = 0.1 \text{ mM}$)

3.2. Discussion

3.2.1. H₂O₂ activation by metal ion catalysts

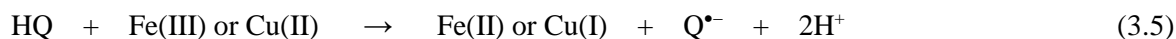
The Fe(III)/H₂O₂ and Cu(II)/H₂O₂ system is already studied to produce reactive oxidants via the Fenton(-like) reaction [14]. Under acidic condition (pH ≤ 3), Fe(III) is reacted with H₂O₂ and reduced to Fe(II) (reaction 3.1). Fe(II) produced by reaction 3.1 is oxidized to Fe(III) by H₂O₂, producing hydroxyl radical ([•]OH) (one-electron transfer reaction); a powerful oxidant (reaction 3.2) [16]. Under circumneutral pH condition (pH ≥ 5), on the other hand, Cu(II) is reacted with H₂O₂ and reduced to Cu(I) (reaction 3.3). Cu(I) is reacted with H₂O₂ and this reaction produces hydroxyl radical (by the one electron transfer reaction) or high valent metal ion species (Cu(III)); by the two electron transfer reaction) (reaction 3.4) [15,24]. In addition, reaction 3.1 and 3.3 are slower than reaction 3.2 and 3.4.



In basic experiment pH condition in this study (pH 4), reaction 3.1 and 3.3 are very slow. Therefore, the reactive oxidants are hardly produced in a single metal ion catalyst/H₂O₂ systems (Fe(III)/H₂O₂ and Cu(II)/H₂O₂). Because of this factor, there was no noticeable 4-CP degradation by the Fe(III)/H₂O₂ and Cu(II)/H₂O₂ systems (10 % and 3 % degradation, respectively) (Figure 3.1a and 3.1b). In the case of Fe(III)/Cu(II)/H₂O₂ system which degraded 90 % of 4-CP, other factors influenced to 4-CP degradation besides the reaction of the metal ion with H₂O₂, producing reactive oxidants. Details explanation of other factors is described in the next section.

3.2.2. Role of 4-CP degradation products; hydroquinone and 1,2,4-benzenetriol

Earlier studies described that Fe(III) and Cu(II) is reduced to Fe(II) and Cu(I) by the reaction with hydroquinone (HQ) (reaction 3.5) [29,30]. Then, the HQ is oxidized to the semiquinone radical (Q^{•-}), which is also oxidized to benzoquinone (BQ) by O₂ (reaction 3.6).



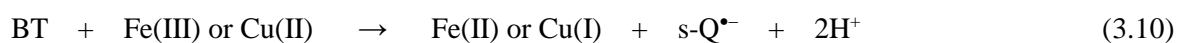
According to reaction 3.5 and 3.6, the production of BQ is explained on phenol and 4-chlorophenol degradation (Figure 3.13). Experimental result in Figure 3.13, the production of BQ on phenol degradation is more than on 4-CP degradation. That is because phenol is sequentially degraded to HQ and 4-CP is degraded to HQ or 1,2,4-benzenetriol (BT).

The BT is known to have the characteristic of autoxidation, which is the process of reacting with

O₂, producing reactive oxygen species (superoxide radical anion (O₂^{•-}) and H₂O₂) [31]. The BT is oxidized to the semiquinone radical (s-Q^{•-}, is different from Q^{•-} mentioned in reaction 3.5 and 3.6) by the reaction with O₂ (reaction 3.7). Subsequently, semiquinone radical reacts with O₂ or O₂^{•-} to produce 2-OH-benzoquinone (2-OH-BQ) (reaction 3.8 and 3.9).



However, Zhang et al. [31] suggested that Fe(III) and Cu(II) accelerate the oxidation rate of BT approximately double and 11-fold, respectively. In other words, Fe(III) and Cu(II) are rapidly reduced to Fe(II) and Cu(I) by the reaction with BT (reaction 3.10).



As mentioned in section 3.1.4, the reducing power of BT is much higher than of HQ. This can explain how the phenol degradation by the Fe(III)/Cu(II)/H₂O₂ system was lower than 4-CP degradation (basically, phenol is easily degraded in comparison with 4-CP) (Figure 3.10c). Because, the main degradation products of 4-CP are HQ and BT, which more contribute to reducing metal ion catalysts than the main degradation product of phenol (only HQ) (Figure 3.14).

3.2.3. Mechanisms of 4-CP degradation by the metal ion catalyst/H₂O₂ systems

Previous studies suggested that the production of reactive oxidants via Fenton(-like) system is dominated by suitable pH condition [14]. However, the experimental pH condition in this study is inappropriate for degradation of 4-CP by a single metal ion catalyst/H₂O₂ systems. The Fe(III)/H₂O₂ system is predominant under acidic condition (pH 3.0 and 3.5, 100% degradation in 30 min) (Figure 3.1a) [14,15]. Interestingly, after pH 4 range, this system hardly degraded 4-CP (10 % degradation at pH 4 in 2 h). The Cu(II)/H₂O₂ system also degraded 4-CP less than 5 % (3 % degradation at pH 4 in 2 h) (Figure 3.1b). Although the degradation of 4-CP by a single metal ion catalyst/H₂O₂ system showed low performance, the Fe(III)/Cu(II)/H₂O₂ system showed very specific consequence that 90 % of 4-CP degraded (Figure 3.1c).

Figure 3.5a shows if Cu(II) existed over a certain amount, the Fe(III)/Cu(II)/H₂O₂ system can almost degrade 4-CP despite only degrading 3 % of 4-CP in terms of Cu(II)/H₂O₂ system. On the other hand, the concentration of Fe(III) had a proportionate effect on 4-CP degradation in the Fe(III)/Cu(II)/H₂O₂ system (Figure 3.5b). In summary, it can be understood that Fe(III) is used as production of hydroxyl radical (•OH) from the reaction with H₂O₂ (reaction 3.1 and 3.2) and both Fe(III) and Cu(II) are reduced to Fe(II) and Cu(I) by HQ and BT which are degraded from 4-CP.

Consequently, the degradation products of 4-CP (HQ and BT) are responsible for the enhancement

of 4-CP degradation by Fe(III)/Cu(II)/H₂O₂ system. The mechanisms of 4-CP degradation by each metal ion catalyst/H₂O₂ system are suggested in Figure 3.15 to 3.17. In the Fe(III)/H₂O₂ system, Fe(III) is reduced to Fe(II) by the reaction with H₂O₂ (slow, rate-determining step; RDS, reaction 3.1), and then the reaction of Fe(II) with H₂O₂ generates hydroxyl radical ($\cdot\text{OH}$) (fast, reaction 3.2) (Haber-Weiss mechanism). 4-CP is oxidized by hydroxyl radical and HQ and BT are formed by sequential oxidation from primary products of 4-CP oxidation. The reaction of 4-CP degradation products with Fe(III) re-generates hydroxyl radical ($\cdot\text{OH}$), which degrades remained 4-CP (Figure 3.15). However, in this system, the rate of 4-CP degradation is just moderate because the rate of Haber-Weiss mechanism is slow at pH 4 and the amount of 4-CP degradation is not enough to produce HQ and BT.

In the case of the Cu(II)/H₂O₂ system, Cu(II) is reduced to Cu(I) by the reaction with H₂O₂ (very slow, RDS, reaction 3.3), and Cu(I) is immediately oxidized to Cu(III) (high valent metal ion species) (reaction 3.4) by the two-electron transfer reaction with H₂O₂. Theoretically, 4-CP is degraded by Cu(III), and degradation products reduce remain Cu(II) to Cu(I), which reacts with H₂O₂ and produces Cu(III) (Figure 3.16). Nevertheless, because reaction 3.3 is much slower than any other reactions, the Cu(II)/H₂O₂ system hardly degraded 4-CP in experimental results.

Lastly, the Fe(III)/Cu(II)/H₂O₂ system is combined with the Fe(III)/H₂O₂ and Cu(II)/H₂O₂ systems (Figure 3.17). At first, the Haber-Weiss mechanism is relatively faster than the mechanism of generating Cu(III) by the reaction with Cu(II) and H₂O₂. Therefore, the Haber-Weiss mechanism is a proper reaction which degraded 4-CP at the beginning. The hydroxyl radical ($\cdot\text{OH}$) degrades 4-CP, and HQ and BT produced by 4-CP degradation reduce metal ion catalysts (Fe(III) and Cu(II) to Fe(II) and Cu(I), respectively). The metal ion catalysts reduced by 4-CP degradation products react with H₂O₂, generate hydroxyl radical and Cu(III). This two-step reaction is the cause to show the characteristic which is similar to a lag phase between 10 and 30 minutes in 4-CP degradation (Figure 3.1). And also, the other experimental results suggest that the rate of which Cu(II) reduces to Cu(I) by 4-CP degradation products is faster than which Fe(III) reduces to Fe(II) (Figure 3.14). As a result, the mechanism of producing Cu(III) by HQ and BT is believed to predominate over producing Fe(II) and hydroxyl radical ($\cdot\text{OH}$).

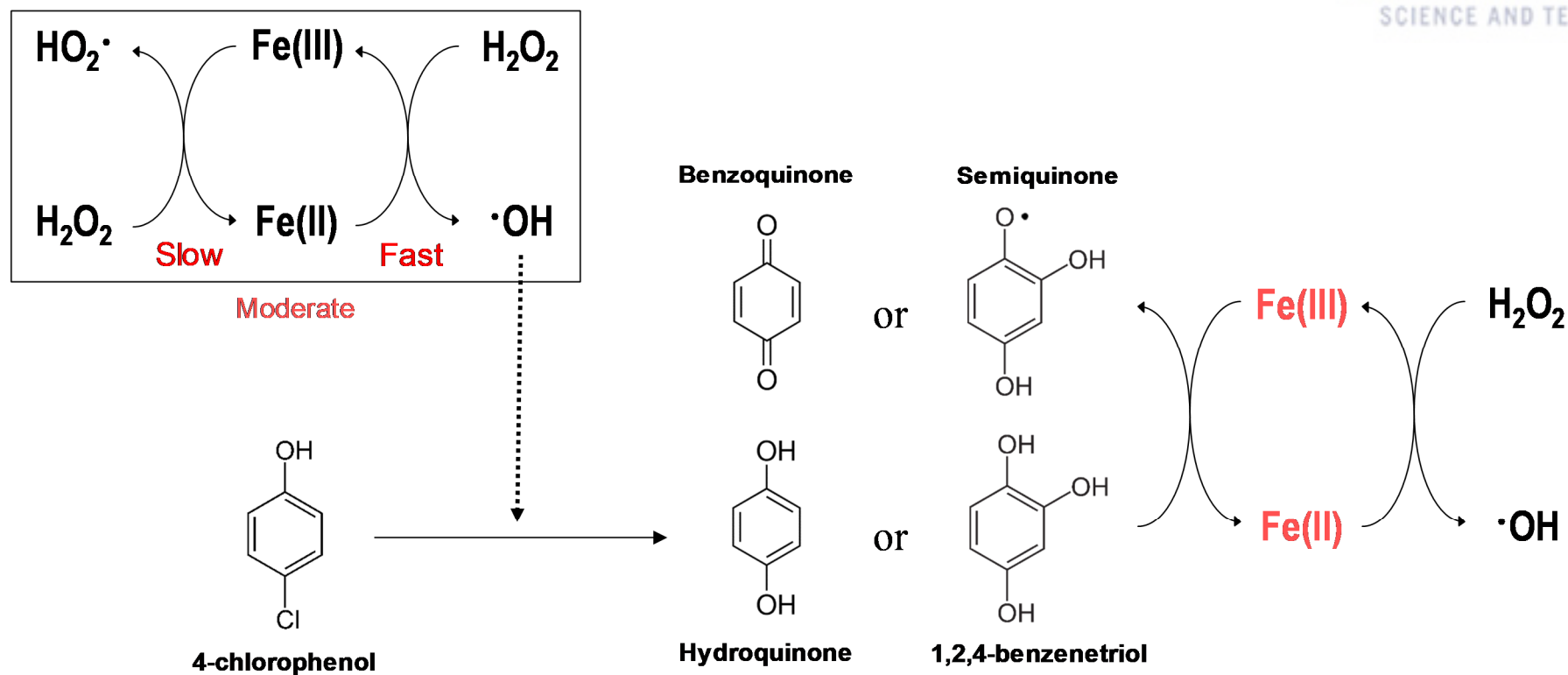


Figure 3.15. Scheme of the mechanism of 4-CP degradation by $\text{Fe(III)}/\text{H}_2\text{O}_2$ system

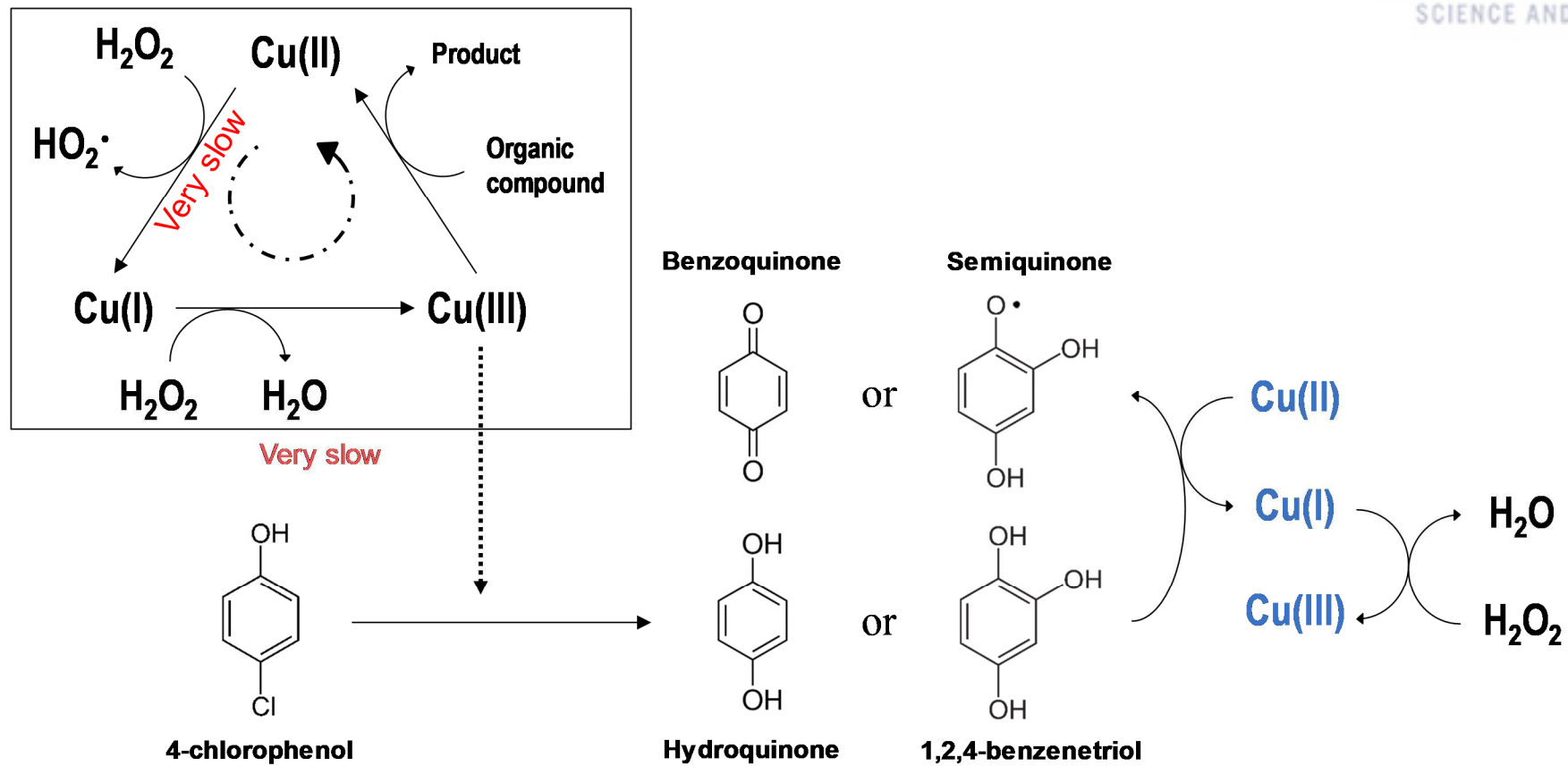


Figure 3.16. Scheme of the mechanism of 4-CP degradation by $\text{Cu(II)}/\text{H}_2\text{O}_2$ system

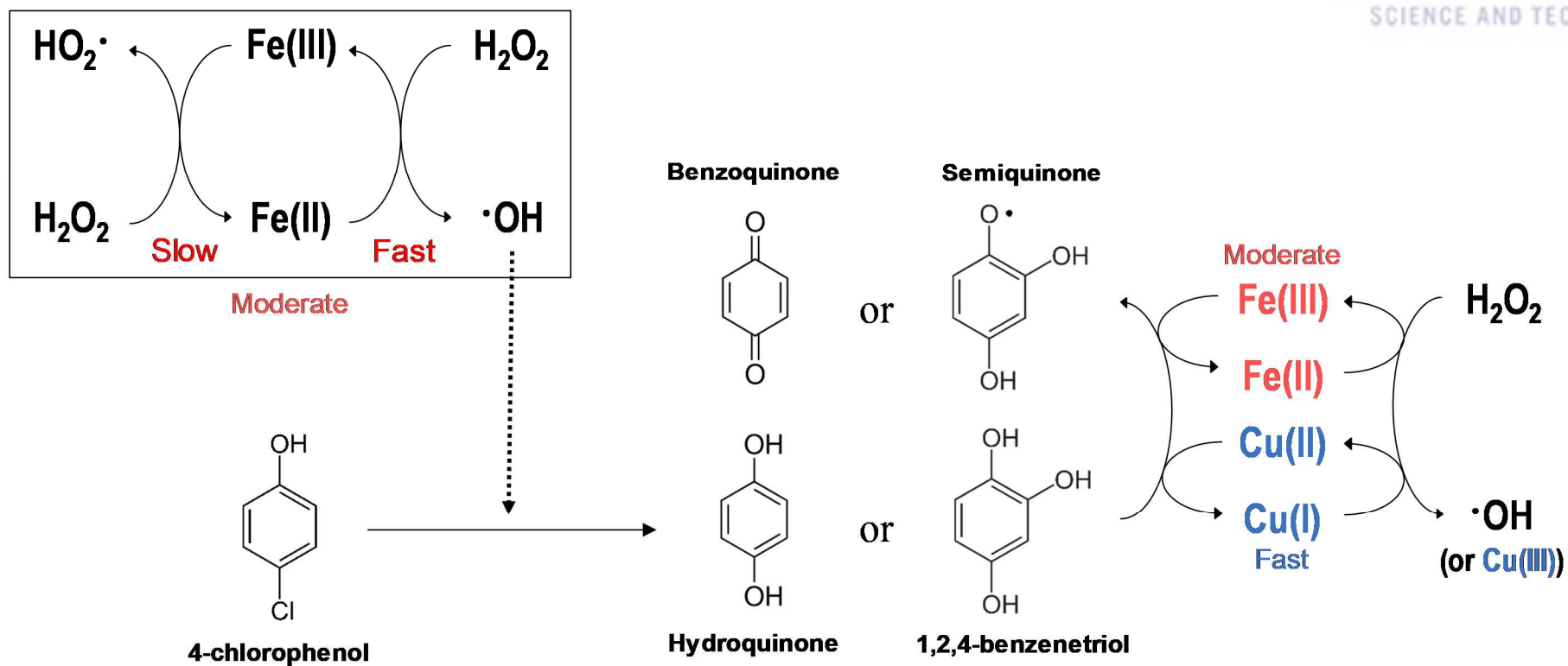


Figure 3.17. Scheme of the mechanism of 4-CP degradation by $\text{Fe(III)/Cu(II)/H}_2\text{O}_2$ system

Chapter 4. Conclusions

This study investigated the 4-CP degradation by the homogeneous Fenton(-like) systems (Fe(III)/H₂O₂, Cu(II)/H₂O₂, and Fe(III)/Cu(II)/H₂O₂) in terms of the enhancement, which is due to coexisting Fe(III) with Cu(II). The experimental results from this study provide a new approach to the effect of degradation products in the degradation of the phenolic compounds.

Haber-Weiss and Cu(III) production mechanisms were difficult to work for producing reactive oxidants (\bullet OH and Cu(III)) at pH 4 because this pH condition is not proper for reacting metal ion with H₂O₂. The Fe(III)/H₂O₂ and Cu(II)/H₂O₂ systems degraded a little 4-CP (10 %, and 3 % in 2 h, respectively). If the production mechanisms of reactive oxidant were slow at the beginning, the amount of 4-CP degradation should be negligible and the production amount of 4-CP degradation products is not enough to produce reactive oxidants.

The Fe(III)/Cu(II)/H₂O₂ system remarkably degraded 4-CP (90 % in 2 h), better than a single metal ion catalyst/H₂O₂ systems. The conclusions of this study are presented as follow.

Firstly, the Haber-Weiss mechanism is worked by Fe(III) reacting with H₂O₂. Then, a little 4-CP is degraded by hydroxyl radical at the beginning; the rate of Cu(III) production mechanism is much slower than Haber-Weiss mechanism while Fe(III) and Cu(II) co-exist. In the first step, hydroxyl radical produced by the Haber-Weiss mechanism may be the main reactive oxidants.

Secondly, there are two main degradation products of 4-CP (hydroquinone (HQ) and 1,2,4-benzenetriol (BT)), which have strong reducing power. HQ and BT produced by a little degradation of 4-CP reduce Fe(III) and Cu(II) to Fe(II) and Cu(I). In this step, Fe(II) and Cu(I) produce reactive oxidant such as hydroxyl radical and Cu(III). When the reactive oxidant is produced by the reaction with HQ and BT, the amount of 4-CP degradation dramatically increases because the generation mechanism of reactive oxidants using HQ and BT is much faster than the mechanism of the first step. The main oxidant of this step is believed to Cu(III) because the reduction rate of Cu(II) by HQ and BT is faster than of Fe(III).

Importantly, the role of Fe(III) contributes to producing hydroxyl radical at the beginning, and role of Cu(II) contributes to producing Cu(III) which is produced by the reaction with HQ and BT. This synergistic effect is believed to be effective in treating phenolic organic compounds. The Fe(III)/Cu(II)/H₂O₂ system shows the great advantages comparing over the traditional Fenton(-like) system based on iron.

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감사의 글

2015년 6월 29일, 학부 1학기가 끝나고 처음 연구실에 인턴으로 출근하게 된 저에게 앞으로 잘해보자고 하시던 이창하 교수님 말씀이 기억에 남아있습니다. 학부과정 당시 스스로가 어떤 것을 공부하고 싶어하는지 모르던 상황으로 앞날을 걱정하고 있을 때, 교수님께서 흔쾌히 진로에 대한 상담을 해 주셨고 환경에 대해 관심을 가져보라 하신 말씀에 흥미를 느껴 환경공학을 공부하다 보니 어느덧 환경공학 석사학위를 취득하게 되었습니다. 인턴 2년, 석사과정 2년 6개월, 총합 4년 6개월이라는 시간동안 실험실 생활을 하며 교수님으로부터 많은 것을 배우고 졸업을 하게 되었습니다. 여러가지 힘든 상황이 많았지만 교수님께서 저에게 주신 가르침과 끝까지 ‘같이’ 해보자는 격려가 없었다면 이자리까지 올 수 없었을 것입니다. 항상 교수님께 부족했던 제자였지만, 사회에 나가 교수님의 가르침을 발판으로 더 나은 사람이 될 수 있도록 계속 노력하겠습니다. 이에 큰 감사를 전합니다.

저의 학위논문심사에 참석해주신 교수님들께도 감사의 말을 전합니다. 학부 과정에서 항상 즐거운 분위기로 가르침을 주셨고 학생들에게 친근감을 주신 조경화 교수님, 수업을 진행하시며 학부생들이 자칫 실수할 수도 있는 공학자로서 지녀야 할 마음가짐들을 가르쳐 주신 이창수 교수님께 감사드립니다.

길다면 긴, 짧다면 짧은 학위기간동안 저에게 무한한 도움을 주었던 선배님들과 동료 및 후배님들께도 감사의 말을 전합니다. 지금의 연구실이 있도록 기반을 잡아 주신 이홍신 박사님, 카리스마와 유머감각을 동시에 가지시고 동료들에게 즐거움을 주신 김형은 박사님, 캐나다에서 연구활동을 이어가시고 계신 이혜진 박사님, 인턴기간동안 제 사수로서 무한한 도움을 주신 Art lab Jesus 김민식 박사님, 항상 웃으며 실험실에 무한한 편안함을 선사해주신 서지원 박사님, Hackipedia에서 각종 지식을 전해주시고 제 사수로서 제가 성장할 수 있도록 많은 도움을 주신 김학현 박사님, 실험실 주당의 원조이자 인턴기간 옆자리에서 도란도란 이야기 꽃을 피워 주신 민정누나, 사회생활에 대한 조언과 앞으로의 진로 및 인생에 대한 많은 상담을 해주었던 준영이형, 랩장으로서 바쁜 와중에도 졸업준비에 어려움 없도록 많은 신경을 써주었던 기명이형, 또래지만 다른 선배님들 만큼 연구에 도움주시고 익살의 끝을 달리시는 카지노 동료 태완이형, 연구실에 전무후무한 캐릭터를 생성하고있는 현석이형, 마음 터놓고 얘기할 수 있고

힘들 때 공감해주던 옆자리 지윤이, 나만큼 연구실에 있었으며 앞으로 더 있을, 항상 밝고 명랑의 끝을 보여주는 음주명치킬러 지혜, 김포공항은 강서구에 있다는 것을 알려준 수연이, 까슬까슬 근육몬 중훈이, 항상 잘 따라주며 응원해주고 연구실생활에 큰 힘이 되어주던 동현이, 긴 시간 껴보진 못했지만 항상 유쾌한 동원이와 Art lab 최장신을 넘겨받게 된 중우, Art lab을 떠나 고려대에서 연구를 진행하고 있는 재민이에게 감사의 인사를 전합니다.

또한, 학부때부터 지금까지 즐거움을 나누고 힘든 일도 함께 나누었던 만년룸메 정신적지주 성우형, 춘데레 슬리프 진태, 프린터맨 호우빠 우정, 학부학생회 및 대학원 학생회를 토대로 정계진출이 목적인 것만 같은 종민, 전자기기 전문가 석진, 교회오빠 진형, 상병제대 민수, 삼성맨 대한, 여수 밤바다 영환, 아직 복무가 남은 홍규장교 성호, 창업에 몰두중인 기범이형과 민수형, 곧 가정을 이루게 될 승민이형, 수도권에서 사회의 일원으로서 커리어를 쌓아가는 종성이형, 준수형, 우인이형에게 감사의 인사를 전합니다.

마지막으로 어떤 선택을 하든지 저를 믿어 주시고 뒤에서 받쳐 주시며 끝까지 응원해 주신 사랑하는 아버지와 어머니께 감사의 말을 전합니다. 더 이상 학생이 아닌 사회 구성원으로서 성장해 나가면서 그동안 저에게 주신 사랑과 도움에 대하여 보답할 수 있는 자랑스러운 아들이 되도록 노력하고 또 노력하겠습니다.

2019년 7월 ART lab에서